Structural evolution of TiO_2 during stoichiometry restoration after reduction

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Titanium dioxide (TiO_2) is a multifunctional material with a wide range of applications in catalysis, chemical sensors, and nano-electronic devices. Its technological relevance stems largely from the moderate chemical reactivity of its surfaces and their intrinsic ability to support and mediate ion migration processes. Furthermore, TiO_2 serves as a prototypical system representing a broader family of mixed transition metal oxides, making it a valuable model.

In most practical applications, the functional performance of TiO_2 is critically dependent on its surface properties. However, these surfaces are typically subjected to a specific preparation/cleaning protocol prior to use, involving intense reduction of the near-surface region followed by reoxidation supported by ionic transport between the bulk and the surface. While often considered a routine surface cleaning procedure, we argue that this process fundamentally alters the crystallographic structure and electronic properties of the material.

In this work, we present experimental results obtained through X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), atomic force microscopy (AFM), and electrical measurements, which together provide a comprehensive view of the complex transformations occurring during the recrystallization of redox-cycled TiO_2. Our findings reveal that these changes are not spatially uniform but instead governed by preferential ion diffusion pathways, which are related with the network of spatial defects present in the real material.